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## FIXATION OF ATMOSPHERIC NITROGEN

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### ABSTRACT OF PAPER

The nitrogen contained in the atmosphere is in an inert form and does not readily lend itself to chemical reactions. To overcome this is the province of "nitrogen fixation."

There are very definite commercial limitations involved in accomplishing this as the world's supply of nitrogen has been readily obtained from vast natural deposits of sodium nitrate in Peru and Chile and the production of a substitute must be at a competitive cost.

The electrical processes for fixing nitrogen have a very low efficiency, due to utilizing thermal energy only.

Combinations of electrical and chemical methods promise the most important developments.

Comparative figures are given showing amount of energy necessary per kilogram of nitrogen fixed, and the general economics of the subject are discussed.

### INTRODUCTORY

IN 1898 Sir William Crooks in his address as President of the British Association, very forcibly pointed out that the commercial fixation of atmospheric nitrogen was one of the greatest discoveries awaiting the ingenuity of chemists. He emphasized with very interesting figures its important practical bearing on the future welfare and happiness of the civilized races. This address brought forcibly to the attention of engineers the fact that the existing sources of fixed nitrogen were limited, and greatly stimulated the efforts of investigators. The problem itself had been worked on for over a century as it was known that nature fixed nitrogen of the atmosphere by means of electric discharges, and Cavendish in 1781 had shown that a small amount of nitrogen was converted into nitric acid in the combustion of hydrogen with oxygen to form water, while Busen in 1877 obtained favorable yields by means of gaseous explosions. The earlier efforts commercially in the art were however largely confined to the fixation of nitrogen for the purpose of manufacturing cyanides, and the earlier bibliography of the subject therefore deals almost entirely with these efforts.

*Commercial Products of Nitrogen.* The three fundamental

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commercial products formed by nitrogen are first, its union with oxygen to form nitrates  $\text{NO}_3$  and nitrites  $\text{NO}_2$ . Second, its union with carbon to form cyanogen  $\text{C}_2\text{N}_2$  and producing cyanides  $\text{XCN}$  and cyanamides  $\text{XCN}_2$ . Third, its union with hydrogen to form ammonia,  $\text{NH}_3$ . From all of the above products there are obtained a large number of derivatives used in the chemical arts.

The most important of all commercial products are the unions of nitrogen with oxygen forming the nitric acid salts of commerce. These are of particular importance on account of the vast natural deposits of nitrate of sodium occurring in Peru and Chile, commonly called Chile saltpeter. Practically, this commodity is the one that sets the price for all other compounds of nitrogen, as it has been mined in Chile since 1830, and during the past 25 years its production has assumed vast proportions, the present annual output amounting to about 2,500,000 tons. This deposit of Chile appeared inexhaustible and therefore there was no occasion for alarm regarding the world's supply of combined nitrogen, but after years spent in exploration work it began to appear that the Chilean deposits would be exhausted before the end of the present century, and since then all other sources of combined nitrogen have received attention.

While there are a few scattered natural deposits other than those in Chile, there is none which has at the present time a chance of competing, most of them being of limited extent and situated in inaccessible regions. In Chile the deposits are easily worked and even after years of careless mining with no effort to effect economies, the present cost of producing nitrate is not excessive, varying from \$10 to \$20 per ton and selling in Liverpool for about \$45 per ton. This leaves a profit of from \$5 to \$10 a ton on the operation after paying the Government of Chile an export tax of about \$12.25 per ton. In the past 30 years this export tax has netted the Chilean Government about \$500,000,000. Of the total production of Chile the United States imports about 600,000 to 700,000 tons per annum the balance being practically all shipped to European countries. Chile saltpeter has sold as high as \$60 a ton but since 1909 when the agreement among the producers expired the price has approximated \$45 per ton f.o.b. Liverpool, making a price of from \$35 to \$40 per ton f.o.b. Chile.

The union of nitrogen and carbon to form cyanides and with hydrogen to form ammonia are two of the earliest forms in which

the combined nitrogen was utilized. Most all animal and vegetable refuse contains ammonia compounds and these were the early sources of ammonia, and animal refuse products such as hides, hoofs and horns were the sources of combined carbon products forming the cyanides. Until the discovery of the McArthur-Forrest process for gold extraction, the markets for cyanides were comparatively limited and there was no great effort made to produce them on a large scale. With the rapid development of this art in the recovery of the low grade gold deposits a sudden impetus was given to the cyanide industry, and large quantities of cyanides are now manufactured from ammonia and metallic sodium. Small amounts of cyanides for industrial purposes are recovered from the gas retort houses but these processes are not generally applied and no particular effort has been made to extend the processes to the recovery of cyanides from by-product coke ovens. The greater portion of the cyanides are manufactured in England and Germany and some 20,000 tons per annum are exported annually by these two countries. As the cyanides of sodium and potassium for gold recovery purposes sell from \$300 to \$400 per ton, they represent one of the highest prices of nitrogen directly combined with a simple element.

The third great commodity of commerce, ammonia, is utilized extensively in industrial arts but in addition has been used for many years as a fertilizer. The annual production of sulphate of ammonia now amounts to about 1,250,000 tons and the Liverpool price approximates that of sodium nitrate, varying from \$45 to \$60 per ton. Practically all of this sulphate of ammonia is manufactured from coal distillation either from gas house retorts or by-product coke ovens, up to the past year there having been practically no process in operation for the direct synthesis of ammonia from its compounds.

All the older retort processes for the manufacture of gas, recover ammonia by washing the illuminating gas with water. All by-product coke ovens likewise treat the by-product gas for the recovery of ammonia. American coals run from 0.9 per cent to 1.4 per cent nitrogen or from 18 to 28 lb. (8.1 to 12.7 kg.) of nitrogen per ton of coal. In the distillation of this coal about 20 per cent of the nitrogen is recovered from the gases of distillation so that from  $4\frac{1}{2}$  to 7 lb. (2.1 to 3.2 kg.) of ammonia are recovered per ton of coal distilled; this ammonia when united with sulphuric acid forms sulphate of ammonia, giving a yield



of from 18 to 28 lb. (8.1 to 12.7 kg.) of sulphate of ammonia per ton of coal distilled. Weak solutions of ammonia water are concentrated from the gas house retorts and the ammonia distilled from this water by breaking down the ammonia contents with lime, the pure ammonia then being united with sulphuric acid. In many of the coke oven plants the sulphate is formed directly by passing the gases into sulphuric acid forming the ammonia sulphate by a direct process.

In general it costs about \$15 per ton of ammonia sulphate to manufacture the sulphate from the ammonia, so that if ammonia sulphate is selling for \$45 per ton, \$15 of this is represented in the cost of sulphuric acid and the manufacturing, making the net ammonia cost with profit \$30 per ton of sulphate or as the nitrogen content of the sulphate amounts to 21 per cent, the nitrogen represents an actual value of 7 cents per pound. With the great increase in the number of by-product coke ovens, there has been a greatly increased quantity of ammonia sulphate manufactured, and it would seem that under these conditions the price of ammonia sulphate will tend to diminish rather than to increase. The actual cost to the by-product coke oven plants recovering the ammonia, in addition to the \$15 for manufacturing the sulphate of ammonia, will approximate \$10 per ton, and if there is any profit to be obtained from the sale of ammonia, they can afford to recover it at this figure.

Another source of ammonia by coal distillation is from producer gas generated on what is known as the Mond system. In this process steam is admitted to the producer in excess, so that the temperature is not permitted to rise to a point where the ammonia liberated by the fuel is decomposed. This excess of steam tends to protect the ammonia and it is recovered from the producer gas by washing. In this process not only the ammonia carried in the volatile products is recovered but also a large percentage which ordinarily remains in the carbonaceous residue of the coke oven and gas house retort. As ordinarily distilled about 50 per cent of the total ammonia of the coal remains in the coke residue and is not recovered. In the producer where this coke is consumed in the presence of steam the total percentage of recovery may be as high as 75 per cent of the theoretical nitrogen contained in the coal, so that from 15 to 20 lb. (6.8 to 9.1 kg.) of nitrogen may be recovered, or in terms of ammonia sulphate, from 60 to 80 lb. (27.2 to 36.2 kg.) of ammonia sulphate may be obtained per ton of coal consumed in the producer.

This type of producer has not been extensively utilized in America as the expense of installation is increased by the necessity of washing a very large volume of low grade gas, the volume of gas per ton of coal consumed in the producer being about 130,000 cu. ft. against about 10,000 cu. ft. per ton of coal as distilled in the coke oven.

A number of these plants have been installed in England and on the continent, but the aggregate of the ammonia sulphate produced is not large as compared to that from coke ovens and gas house retorts.

*Available Nitrogen in Commercial Products.* The question of the available nitrogen in the various compounds has in a measure determined the price of the product, the utilization in the fertilizer art being practically the basis of fixing the price. For a number of years it has been assumed that the selling price of combined nitrogen would be from 12 cents to 13 cents a pound. Thus Chile saltpeter being about 95 per cent pure nitrate of soda would have a theoretical nitrogen content of about 16.5 per cent or corrected for impurities would have about 15.5 per cent nitrogen.

As the cyanides until recently were not used directly in the fertilizer art and were combined with more expensive products, their price has not been regulated by their content of combined nitrogen. The ammonia used in the fertilizer art is almost entirely used as sulphate of ammonia, on account of the cheapness of the commercial sulphuric acid and the ease of manufacture, and this product would therefore have a theoretical content of 21 per cent of nitrogen.

The above nitrogen products may be considered the fundamental commercial forms in which combined nitrogen enters the market, and while the fertilizer industry fixes the price of combined nitrogen, it is only one of the many industries in which vast quantities of nitrogen are utilized. Thus about 50 per cent of all the Chile saltpeter imported in this country is used in the manufacture of explosives, while an additional 25 per cent is utilized in the arts requiring nitric acid. Of the ammonia sulphate, a very large percentage is used directly as fertilizer, though there is a very considerable demand for use in chemical industries and such commercial applications as anhydrous and aqueous ammonia used in the refrigeration art. Practically all explosives have utilized nitrogen compounds as a principal ingredient. The earlier black gun powder having used Chile

saltpeter, charcoal and sulphur and the later so-called smokeless powder utilizes the oxygen carrying property of nitrogen as well as the inherent molecular energy in the production of such high explosives as nitroglycerin, cordite, lydite, mellenite, gun cotton and various other nitro-cellulose compounds, and modified explosives used in industrial work, such as dynamite and various blasting powders.

*Fixation Processes.* In considering the fixation of atmospheric nitrogen from a commercial standpoint, the limitations will be imposed by the selling price of the natural product from Chile, covering nitrate compounds, and the selling price of ammonia sulphate as obtained from coal distillation, affected as these prices will be by the manufacture of ammonia from atmospheric nitrogen.

In competition with the above sources of nitrogen there has been the constant effort toward the fixation or rather the utilization of some of the vast quantity of atmospheric nitrogen surrounding us.

A list of these fixation processes would contain the names of hundreds of investigators, and from the past twenty years of effort there may develop processes which at present are still experimental; but of the various processes which have reached the state of commercial application there appear to be four distinct lines of development.

First. The production of nitric acid directly from the atmosphere by means of the electric arc. In this process the nitrogen of the atmosphere is directly combined with its accompanying oxygen without utilizing any other chemical substances, the process consisting essentially of a powerful arc furnace through which air is forced, causing at this high temperature the nitrogen to combine with the oxygen forming nitric oxide, NO.

Second. Methods of fixing nitrogen by means of electric furnaces or combustion where the energy of chemical combination is utilized causing the nitrogen to combine with some substance with which there is a pronounced energy of chemical combination. These processes include furnaces utilizing calcium carbide with which nitrogen readily combines to form calcium cyanamide  $\text{CaCN}_2$ , and various processes for making combinations of nitrogen and a basic or alkaline earth metal such as calcium nitride,  $\text{Ca}_3\text{N}_2$ , or magnesium nitride,  $\text{Mg}_3\text{N}_2$ , or aluminum nitride,  $\text{AlN}$ , the chemical action usually forming a nitride or carbo-nitride.



Third. Processes for producing ammonia,  $\text{NH}_3$ , directly from nitrogen and hydrogen. These include the effort to use the various forms of electric discharge by which the nitrogen molecule may be decomposed and in the presence of hydrogen, form ammonia. As ammonia decomposes at a very low temperature (500 to 1000 deg. cent.) only the silent discharge seems available, and the yields are not commercial. The most promising of all direct ammonia processes seems to be that of Haber. In this process, a catalytic agent is used and under a heavy pressure the nitrogen molecule is decomposed and united to the hydrogen thus forming ammonia. Salts of uranium seem to be preferred as the catalytic agent and have the power of acting on nitrogen at a temperature of about 500 deg. cent.

Fourth. Production of a high temperature by combustion utilizing either catalytic agents or simply by producing a high temperature by means of the explosion or combustion of gases directly combining the nitrogen and oxygen to form nitric oxide,  $\text{NO}$ . This method early used by Bunsen in the combustion of hydrogen to form water has been applied to coke oven gases by Hausser. A bomb is used and the mixture of gas and air is fixed electrically, the small amount of  $\text{NO}$  formed is recovered and converted into nitric acid,  $\text{HNO}_3$ .

The chemical form in which the commercial supplies of combined nitrogen appear on the market is due largely to existing commercial conditions. The nitric acid combined as sodium nitrate occurs in this form simply on account of being naturally produced in this form. The ammonia appears on the market as ammonia sulphate largely on account of the cheapness with which sulphuric acid can be obtained, and the widely distributed plants for its manufacture, making it one of the cheapest and most convenient forms of combining with ammonia. It is probable that in commercial nitrogen fixing plants, if both ammonia and nitric acid are manufactured, one of the most convenient forms for marketing this product will be by using nitric acid in place of sulphuric acid making ammonia nitrate,  $\text{NO}_3\text{NH}_4$ . This product is on the market at present but is only manufactured from sodium nitrate and from ammonia, or in some of the plants where nitric acid is manufactured, ammonia is shipped to the nitric acid plants to be manufactured into ammonia nitrate. The advantage of ammonia nitrate is that it has a nitrogen content of 35% in this respect being a much more concentrated nitrogen product either for the processes of manu-

facturing other compounds of nitrogen or for use in the fertilizer industry.

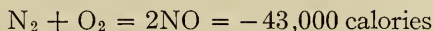
*Physical Limitations and Those Fixed by Natural Sources.* The competition with natural sources will fix the commercial limitations or selling prices for these various nitrogen compounds and in considering the possible developments of the processes it will be interesting to see to what extent they have definite theoretical limitations, as these will greatly affect any comparison of possibilities. Before considering in detail these processes we might endeavor to investigate whether our present conception of the physical and chemical reactions involved impose real limitations, or whether there is an uncertain boundary which further developments may encroach upon, perhaps thus continually improving the efficiency and possibilities commercially. If for instance the nitric oxide processes which utilize only 2 per cent to 4 per cent of the energy supplied to the furnace are limited to this amount by the inefficiency of the apparatus, there is much greater possibilities of development than would be the case if the process has definite physical or thermodynamic limitations, and the present apparatus utilizes a favorable percentage of this possible ultimate limit. To some extent these theoretical limitations are not always sharply defined, and research will extend this horizon, but we may determine some of these limitations quite definitely.

## II. THEORETICAL LIMITATIONS

As we are considering this subject from its engineering aspects, it may be excusable to examine some of the theoretical limitations imposed by the laws of physical chemistry, and in reviewing what may be termed elementary formula, it is interesting to note that the investigation of these theoretical limitations has been of fundamental importance to physical chemistry in extending the application of the laws of chemical dynamics.

*Molecular Inertness of Nitrogen.* The elements carbon, C, and nitrogen, N, possess a marked similarity in the fact that the molecule of each is composed of two or more atoms united together with a bond representing a large amount of energy. Nitrogen, having an atomic weight of 14, has a normal molecular weight of 28, indicating two atoms to the molecule, and in this molecular form it occupies 79.2 per cent of the volume of the earth's atmosphere. To separate this molecule into its constituent atoms and cause these atoms to combine with other

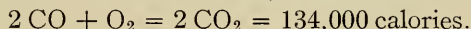
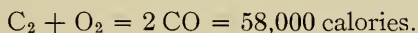
elements is the problem of the fixation of nitrogen. Unless combined in the atomic form, the enormous bond between the atoms causes them to combine upon themselves into the inert form of molecular or atmospheric nitrogen. The ordinary compounds of nitrogen are formed only by the expenditure of a large amount of energy, the union of molecular nitrogen,  $N_2$ , and molecular oxygen,  $O_2$ , to form nitric oxide,  $NO$ , being represented by the formula,



Or in other words, to form one gram molecule of nitric oxide,  $NO$ , requires the expenditure of energy amounting to 21,500 calories.

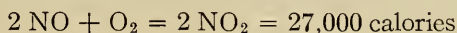
The general similarity to carbon in this molecular inertness makes an interesting comparison.

Thus



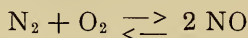
The formation of one gram molecule of  $CO$  therefore represents the liberation of 29,000 calories while the formation of one gram molecule of  $CO_2$  from  $CO$  represents 67,000 calories or a total of 96,000 calories in the formation of  $CO_2$  from the original elements  $C$  and  $O$ . When amorphous carbon therefore is caused to assume the gaseous condition and unite with a molecule of oxygen there is liberated 29,000 calories but after assuming this condition in which the molecule is no longer composed of the inert carbon molecule, a second gram molecule of oxygen unites with the  $CO$  and liberates 67,000 calories additional. The second molecule of oxygen therefore liberates 38,000 calories more than the first molecule, and as the oxygen molecules were alike this energy represents the bond uniting the carbon atoms and the energy necessary to break down the bond between these atoms and produce a gaseous condition from the amorphous condition.

Returning to the nitrogen molecule, it is apparent that the formation of the gram molecule of  $NO$  requires 21,500 calories in comparison to carbon liberating 29,000 calories to form  $CO$ ; that is, the nitric oxide reaction is endothermic while the carbon monoxide reaction is exothermic. Upon adding a second molecule of oxygen to the nitric oxide to form the peroxide we find,



or 13,500 calories per gram molecule are liberated after previously expending 21,500 calories to form NO. Since there is liberated only 13,500 calories upon adding a second molecule of oxygen, the net energy required to form the NO<sub>2</sub> would be 8000 calories. The first molecule of oxygen required 21,500 calories whereas the second required only 8000 calories, so that 13,500 calories were required by the nitrogen molecule to prepare it for combination with the oxygen.

*Dynamic Equilibrium.* These heats of combination developed by the atoms combining upon themselves indicate a very stable or inert molecule, and in liberating this energy to assume this more stable form the forces exerted are of large magnitude. It is readily apparent from this for instance how carbonaceous gases can readily form soot and cinders and other amorphous forms, when the union with oxygen is disturbed, as the tendency of the atoms to unite with oxygen or to form carbon molecules will depend upon an adjustment of the surrounding conditions. This ever-changing condition of equilibrium constitutes the dynamic conception of equilibrium displacing the static equilibrium of the older theories of chemistry. In order to more carefully consider some of the theories that have been advanced it may be of interest to follow further some of the concepts of physical chemistry. The fact that the nitrogen atom has this strong tendency to combine upon itself with a liberation of energy greater than the combination with the oxygen atom, indicates that in any reaction when the combination with oxygen has made possible a changing of the atoms there will be continuously in progress an action and a reaction and the equilibrium will be indicated by the expression



the sign of equality being displaced by the two arrows indicating that the action proceeds in each direction, that is, it is a reversible reaction, and the equilibrium will be dependent upon conditions, the two most important conditions being temperature and the active masses of the substances present. Considering first the effect of the active masses present, if it be assumed that the collision of molecules causes the re-arrangement of the atoms comprising the molecule, and that of these collisions only a certain number will cause the re-arrangement to proceed in one direction, the re-arrangement will be greater the more fre-



quently the collisions take place, there being some ratio for each individual case, and the collisions possible will obviously be proportional to the concentration present, that is, the collisions will be proportional to the number of molecules present. With two substances present, the collisions will be proportional to the molecules of each present and hence to their product.

*The Velocity Coefficient.* If  $C_1$  and  $C_2$  represent the special concentration of gram molecules present, the velocity of the reaction will be proportional to  $C_1 C_2$  or the velocity  $V$  of the reaction will be

$$V = C_1 C_2 k$$

where  $k$  is a constant or coefficient to be determined for the given temperature. This velocity of reaction will proceed each way in reversible reactions, the concentrations of the molecules in the reverse action being represented by  $C_1'$  and  $C_2'$  and the velocity of reaction by  $V'$ , the velocity of the reaction in the reverse direction will be

$$V' = C_1' C_2' k'$$

where  $k'$  is the velocity constant to be determined for the reverse reaction.

*The Equilibrium Constant.* The chemical driving force for any reaction will continually diminish as the reaction approaches equilibrium, or the velocity of the reaction will diminish as equilibrium is approached, and when equilibrium is reached  $V$  will equal  $V'$  and

$$k C_1 C_2 = k' C_1' C_2'$$

This dynamic equilibrium indicates that as much reactive substance is being formed in a given time as is being decomposed, and a fixed relation therefore results, but the reactions have not ceased, only the velocities have equalized, and the driving chemical forces are incapable of making any further change in the reacting substances unless the velocity in one direction or the other is changed. In this state of equilibrium the ratio between the velocity coefficients or constants is

$$\frac{k_1}{k} = \frac{C_1' C_2'}{C_1 C_2} = K = \text{equilibrium constant.}$$

Or, as the concentration or active mass in any reaction increases, the velocity coefficient increases, and for each change in equi-



rium due to temperature change, there is a definite concentration ratio represented by this equilibrium constant  $K$ .

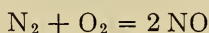
*Partial Pressures.* If the concentration of a given molecule is  $C$  and the collisions of the molecule are proportional to this concentration, if there are two molecules the collisions between the two similar molecules will be  $C$  times as great as one molecule, or  $C^2$ . As the total pressure of a mixture of gases is the sum of the pressure of each gas, and by Avagadro's hypothesis the pressure is proportional to the number of molecules in the given space, the concentrations instead of being represented by gram molecules  $C$  may be expressed as partial pressures  $p$ , and equilibrium will be represented by the ratio of the partial pressures of the gases. Thus two molecules of NO will have the pressure  $p_{\text{NO}}^2$  while  $p_{\text{N}}$  and  $p_{\text{O}}$  may represent the pressure of N and O. At equilibrium the constant  $K$  will then become

$$K = \frac{p_{\text{NO}}^2}{p_{\text{N}} p_{\text{O}}}$$

and for any pressure and volume the familiar equation

$$PV = RT$$

will represent the work done. Where  $P$  is the pressure,  $V$  the volume,  $R$  the gas constant, and  $T$  the absolute temperature. The work done in the reaction



will consist in taking one molecule of  $N$  from the pressure  $p$  and transferring to the pressure  $P$  also one molecule of  $O$  from the pressure  $p$ , to pressure  $P$ , and offsetting this work will be the transferring of two molecules of NO from pressure  $P_{\text{NO}}$  to  $p_{\text{NO}}$  when the pressure of a gas at constant volume is increased by the infinitely small amount  $dp$ , the corresponding work done  $dA$  will be

$$dA = dpV$$

*The Maximum Work.* If we substitute for  $V$  its value from the equation

$$pV = RT$$

we have

$$V = \frac{RT}{p}$$

and

$$dA = \frac{RTdp}{p}$$

and for the work done between the limits of pressure  $p$  and  $P$  we have

$$A = RT \int_P^p \frac{dp}{p} = RT \ln \frac{p}{P}$$

where  $\ln$  is the natural logarithm. For the work done in forming the NO at a temperature  $T$ , we will have



$$A = RT \ln \frac{p_N}{P_N} + RT \ln \frac{p_O}{P_O} - 2 RT \ln \frac{p_{NO}}{P_{NO}}$$

or simplifying and assembling the initial pressures and the final pressures in separate terms, we have for constant temperature

$$A = RT \ln \frac{p_N p_O}{P_N^2 P_O} + RT \ln \frac{P_{NO}^2}{P_N P_O}$$

But the first term represents the initial pressures or the work done on the initial condition of the materials, and we are not called upon to furnish this energy, the change of energy being represented only by the second term

$$RT \ln \frac{P_{NO}^2}{P_N P_O}$$

This quantity  $\frac{P_{NO}^2}{P_N P_O}$  is, however, the ratio of pressures or concentrations represented by the equilibrium constant  $K$  and hence the work done at any given temperature may be represented by the equation

$$A = RT \ln K$$

Vant Hoff has applied this type of fundamental equation to a wide range of reactions and by means of the second law of

thermodynamics has made it applicable to temperature and concentration changes in which the latent energy plays an important part, for in these reactions the product of the specific heat by the temperature no longer represents the heat transfer.

*Vant Hoff's Fundamental Equation.* The second law of thermodynamics expresses the relation of  $A$ , the maximum work possible at a temperature  $T$ , and  $U$ , the decrease in energy of the system in relation to the ratio of change of  $A$  with the temperature  $T$ , the equation being

$$A - U = T \frac{dA}{dT}$$

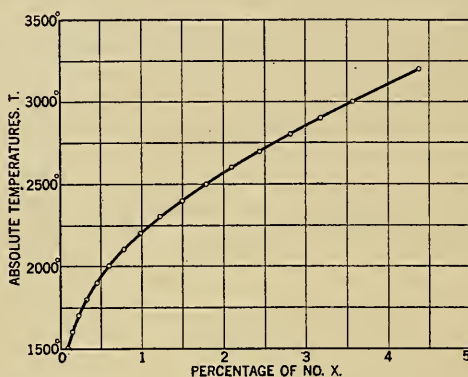


FIG. 1

Substituting in this the value of  $A$  and  $\frac{dA}{dT}$  obtained from the equation

$$A = RT \ln K$$

we have when both  $A$  and  $\ln K$  change with the temperature  $T$

$$\frac{dA}{dT} = R \ln K + RT \frac{d \ln K}{dT}$$

and hence

$$U = - RT^2 \frac{d \ln K}{dT}$$

which is Vant Hoff's fundamental equation for chemical reactions in which the heats of reaction  $U$  are important factors and both the temperature and concentrations may be variable.

The quantity  $U$ , which in thermodynamics represents the decrease in energy of the system, may here represent the energy of chemical combination, which changes very little with changes of temperature and is generally designated as  $Q$ , and in the case of nitric oxide it has the value 21,500 calories per gram molecule; so the equation becomes

$$43,000 = -RT^2 \frac{d \ln K}{dT}$$

and when using the air as a source of nitrogen in which the nitrogen content is 79.2 per cent and the oxygen 21.8 per cent and letting  $x$  represent the percentage of NO formed, as  $\frac{1}{2}x$  will be from the nitrogen and  $\frac{1}{2}x$  from the oxygen, the equilibrium constant  $K$  will be

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right) \left(20.8 - \frac{x}{2}\right)}$$

*Nernst's Determinations of Equilibrium.* Nernst and his assistants determined  $x$  for a number of temperatures, the calculated and observed values being as follows:

T.	$X(\text{Obs.})$	$X(\text{Calc.})$	Observer
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023 bt. 0.52 and	0.80	0.64	Jellinek
2033	0.64	0.67	Nernst
2195	0.97	0.98	Nernst
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	Nernst-Finckh

Nernst's calculations of  $x$  or equilibrium volumes in per cent of NO, using air at temperatures of 1500 deg.  $T$  to 3200 deg.  $T$  are plotted in Fig. 1.

*Rapidity of Dissociation.* Nernst and Jellinek also determined the rapidity with which the NO is decomposed or dissociated at the various temperatures and these experiments showed that the tendency of NO to revert to molecular N and O is very slight below a temperature of 1500° C but increases very rapidly with the temperature so that the time of withdrawing the products through the varying zones of heat in the electric arc is sufficient to effect a large amount of dissociation. In order

to avoid this dissociation a rapid movement of the air through the arc or the arc through the air is desirable, and this in turn causes increased radiation and convection losses, so the maximum possible temperature of the arc is not obtained and hence there are imposed very distinct limitations to the yield of NO.

*Haber's Theory of Ionic and Electronic Collisions.* Haber and Koenig investigated the possibility of utilizing lower temperatures in the arc to avoid dissociation by enclosing the arc in a water cooled quartz tube whereby moderate temperatures were preserved. In place of the molecular collisions we have assumed above as due to the thermodynamic condition of the gas, they used a vacuum and endeavored to utilize the kinetic energy from the rapid motion of the ions and electrons liberated by the arc stream under these conditions. Habor considered it possible to increase the thermodynamic concentrations about 50 per cent. His tests indicating that using a temperature of 3000 deg. cent. it was possible to show 10 per cent concentrations of NO which would correspond to a temperature under the thermodynamic equilibrium of 4300 deg. cent. Haber gives a table showing the effect of various mixtures of N and O when working with the increased mean free path of the molecules due to a vacuum of 100 mm. of mercury. In his work Haber prefers to use the square root of the equilibrium constant  $K$  we have used above, thus enabling the partial pressures of the resulting substances to be read direct, while the partial pressures of the ingredients are expressed as square roots of the pressures.

Haber's table for a pressure of 100 mm. is as follows:

Gas mixture				K = (NO) $(N_2)^{\frac{1}{2}}(O_2)^{\frac{1}{2}}$	Thermodynamically calculated absolute temperature by	
	O <sub>2</sub> per cent	N <sub>2</sub> per cent	percent NO			
					Haber	Nernst
Air	20.9	79.1	9.8	0.284	4365	4334
Half-half	48.9	51.1	14.4	0.337	4686	4650
mixture	44.4	55.6	14.3	0.337	4686	4650
Reversed air	75.0	25.0	12.8	0.357	4805	4767
mixture	81.7	18.3	12.1	0.397	5042	5000

The yields of NO per kilowatt hour obtained by Haber were unsatisfactory and the complications of small water cooled tubes



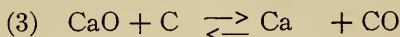
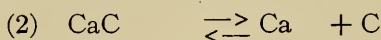
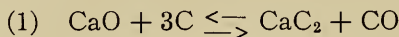
and working under a vacuum of 100 mm. have not justified commercially the higher concentrations of NO he obtained.

*Commercial Processes now in Use have Distinct Limitations.* We may assume that up to the present the processes in commercial use are limited strictly by the thermodynamic equilibrium of the Vant Hoff equation. As the volume of gases when working with low concentrations of NO are considerable, the radiation and convection losses as well as the transfer of sensible and latent heat from the arc to the gases lower very materially the temperature of the arcs, and the yields therefore indicate an average working temperature of 2200 deg. cent. to 2500 deg. cent., or concentrations of 1.5 per cent to 2 per cent NO when working with air. These theoretical limitations of the direct process of forming NO have therefore led to many efforts to dissociate the nitrogen molecule by other means.

*Sources of Chemical Energy.* Naturally the sources of chemical energy have offered a most fruitful field but like the synthesis of carbon compounds a considerable elevation of temperature is necessary before the chemical energy becomes effective enough to break the bond of the nitrogen molecule. At these elevated temperatures practically all elements or compounds which release sufficient energy to combine with nitrogen have a greater combining power for oxygen so the processes cannot be conducted with air but involve the separation of the nitrogen from the oxygen of the air as a preliminary step. The compounds of nitrogen thus formed do not therefore include the oxides of nitrogen. The common elements exhibiting the most pronounced tendency to combine with nitrogen are calcium (Ca), magnesium (Mg), aluminum (Al), boron (B) etc. The carbides of a large number of metals also exhibit a pronounced tendency to combine with molecular nitrogen, when heated.

The great advantage from a theoretical standpoint in utilizing these processes is that the reaction with nitrogen may be made more complete as equilibrium may be continually disturbed by withdrawing the compound of nitrogen formed or by presenting to the nitrogen to be combined fresh combining surfaces of the substance and the action may be caused to proceed practically quantitatively thus avoiding heating large quantities of materials which are inert to the reaction. A vast field of research is opened by these possibilities as very few of the equilibrium figures have been determined, and it is almost certain that direct combustion methods may eventually be evolved along these lines.

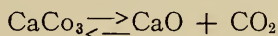
The experimental data are so meager that no theoretical limitations can be placed. The reactions assume unusual importance however on account of a wide application in the arts. This may be best illustrated by considering the formation of calcium carbide,  $\text{CaC}_2$ , in relation to its three reversible reactions, namely



There are here six substances, some in solid form, some in liquid and some gaseous (molecular and atomic) and it is evident that the temperature will have a marked influence on the equilibrium which will exist, and the reaction will be greatly affected by very minute changes, for the partial pressure of the gases will be suddenly changed by such conditions as the carbon released in a gaseous state immediately combining to form amorphous carbon, or the metallic calcium vapor combining with the oxygen released by the CO to form calcium oxide which immediately precipitates as a solid. The fact that calcium oxide which is most refractory, can be vaporized at a temperature of 1600 deg. cent. to 1800 deg. cent. in the sense that the calcium is vaporized and decomposes CO to again precipitate CaO is one of the actions similar to the fumes in smelting furnaces which accounts for a heavy loss of metal at temperatures not ordinarily capable of producing fusion. When nitrogen is inserted in a reaction of this kind, there are immediately formed complex carbon-nitrogen compounds, but the action of the oxygen present is to dissociate these, allowing the nitrogen to combine into the molecular form and the metal to precipitate from the fume as a minute particle of metallic oxide, the carbon precipitating as amorphous carbon in the form of soot, as all of these reactions liberate a large amount of energy. The temperature of these reactions is from 1500 deg. cent. to 2000 deg. cent. and is therefore well within the range of combustion methods if the combustion could be in contact with the substances as in the blast furnace, but the presence of the oxygen necessary for combustion prevents the formation of nitrogen compounds.

The effect of partial pressures in these reactions is of fundamental importance. The active mass of a solid is constant and

hence at the boundary surface where the solid and gases meet there is a high velocity of reaction. Equilibrium will be produced either by the solid forming a coating of the compound which will place it in equilibrium or by the pressure of the gases generated from the reaction producing a condition of equilibrium. Taking the familiar calcium carbonate reaction as an illustration,



There being two substances in the solid state and one in the gaseous, the equilibrium constant  $K$  will be

$$K = \frac{\text{CaO} \times \text{CO}_2}{\text{CaCO}_3}$$

where  $\text{CaO}$  and  $\text{CaCO}_3$  are the very slight vapor pressures of the solids, that is the sublimation pressures, which in practice are too small to measure. The pressure of the  $\text{CO}_2$  will be practically the total pressure, and as this varies, the velocity constant  $K$  will vary and hence for any temperature there is but one pressure for equilibrium. LeChatelier measured the temperatures and pressures of the above reaction over a wide range and found a variation in the temperature necessary to produce the reaction of from 547 deg. cent. at 27 mm. pressure, to 865 deg. at 1333 mm., or in other words, equilibrium could be produced through a range in temperature of 60 per cent., and at one point a change of two degrees necessitated a change in pressure of over 10 per cent. in order to restore equilibrium. Rothmund found the equilibrium pressure of  $\text{CO}$  in the carbide of calcium reaction to be 250 mm. at 1620 deg. cent. If the  $\text{CO}$  pressure was raised above the equilibrium figure at this temperature  $\text{CO}$  was absorbed and no carbide was formed. By inserting inert gases so the  $\text{CO}$  was diluted and its partial pressure reduced, the temperature of the formation of carbide was varied over 20 per cent. These results all indicate that for the nitrogen reactions, the actions and reactions must not only be subject to accurate temperature regulation but the partial pressures must be controlled and it is probable that definite zones of reaction must be maintained. The present commercial applications such as the Serpek and cyanamide process prepare the compounds of nitrogen by causing the nitrogen to react largely with the solid masses and thus avoid many of these complications due to the

vapor processes, or variable minute pressures of sublimation.

By substituting the resistance furnace for the arc and reducing the metals in the presence of nitrogen thus forming nitrides or forming carbides and treating these in the presence of nitrogen, there have been developed a number of processes which have been commercially applied.

### III—DESCRIPTION OF PROCESSES

Three processes which have been commercially applied for directly preparing nitric acid from atmospheric nitrogen are first, Birckland-Eyde; second, the Schonherr; and third, the Pauling. These are diagrammatically shown in Figs. 2, 3, and 5. Fundamentally all operate on the same principle of forcing air into intimate contact with a high-tension arc and withdrawing the product nitric oxide, NO, as directly and rapidly as possible in order to reduce the amount of decomposition of the resulting product. As these processes have been repeatedly described in detail in the technical press, we will confine our attention to general comparisons.

*Birckland-Eyde Process.* The Birckland-Eyde furnace, illustrated in Fig. 2, has been the most extensively used. Its most distinctive features are the use of the magnets *A* which distort the arc into a series of great wheels of flame, extending radially outward from the electrodes *E* located normal to the paper in Fig. 2. The air enters through the conduit *C* and is distributed to the arc through the holes in the firebrick lining. The products are withdrawn from around the periphery at *D*. The voltage of 10,000 volts is reduced by an inductive reactance coil to about 5500 volts across the electrodes. The alternating current of 50 cycles establishes the arc across the U-shaped water cooled electrodes *E*, spaced about 0.3 in. (8 mm.) apart and a flow of current takes place across this ionized path, the electrons formed being repelled by the intense magnet field of the direct current magnets, *A*, and their discharge radially outward causes the arc stream to follow until it is deflected outward in a great semicircle. As its length is thus increased the potential across the electrodes rises and a second arc is established, the effect being to make a series of rapidly expanding arcs which are expanded across the entering air spaces. As the arcs travel radially outward the contact of the ionized arc stream with the incoming air disrupts the nitrogen molecule and causes the formation of NO, and the gaseous products travel rapidly to the



periphery of the furnace where they are withdrawn at an average temperature of about 1250 deg. cent. The earlier Eyde furnaces were of 300 kw. capacity and gave a concentration of about 1.5 per cent NO and a yield of about 500 kg. of nitric acid per kw. per year. The more recent furnaces are of 3000 kw. capacity and give concentrations of about two per cent NO and a yield of 580 to 600 kg. of nitric acid per kw. per year, or 65 to 70 grams of nitric acid per kw-hr.

*Schonherr Process.* The Schonherr furnace (Fig. 3) consists

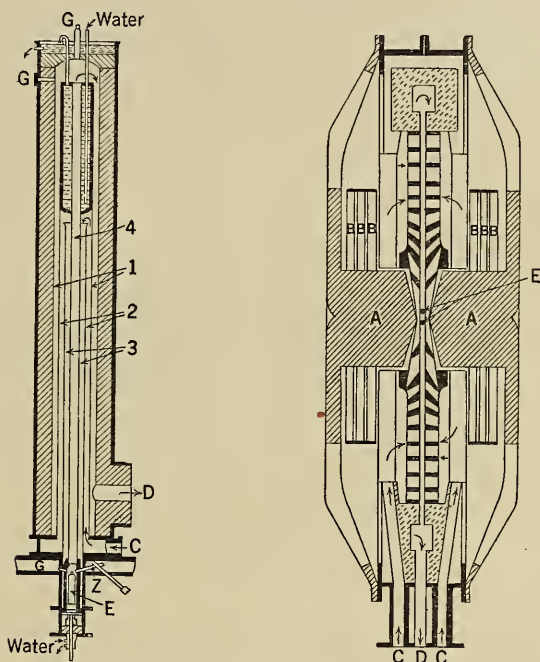


FIG. 2—BIRCKLAND-EYDE FURNACE      FIG. 3—SCHONHERR FURNACE  
A, core; B, windings; C, gas entrance; D, exit.

of a long iron pipe 4 having an electrode *E* inserted in the bottom and the tube itself is the other electrode, the distinctive feature of the process being that an alternating current at 4500 to 5000 volts maintains an arc of from 23 to 25 feet (7 m. to 8 m.) The furnace is started by forming an arc from the lower electrode to the wall of the iron pipe by means of a lever *Z*, a blast of air is then admitted to the pipe, whereupon the ionized gases are caused to ascend and carry with them the arc stream. In this way the arc is caused to travel toward the upper end of the



tube where it is maintained. In practise, the air stream is admitted in a tangential direction causing a whirling motion to be imparted to the air surrounding the arc, this creates a vortex motion causing the arc to be surrounded by the cooler air and thus protects the iron pipe which is wholly unlined. The rapid passage of the air maintains an ionized path for the arc stream and the arc burns quietly. The products are withdrawn from the upper end and pass downward through the passes *I* to the outlet *D*. Previous to being withdrawn they are cooled by the water cooler and are further used to preheat the entering air. The temperature of the exit gases is about 850 deg. cent. Provision is made for preheating the air by passing it upward in

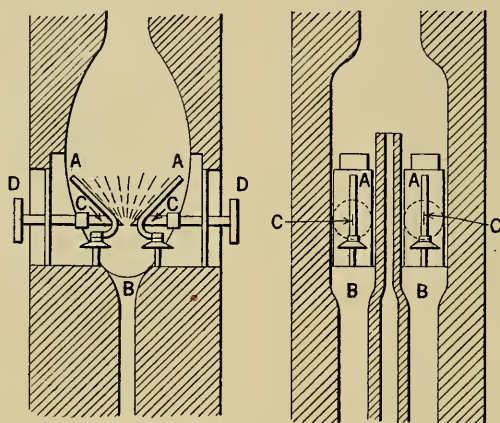


FIG. 4—PAULING NITRIC OXIDE FURNACE

the space 2 of the casing and then downward to a point opposite the electrode. The largest furnaces are of 800 kw. capacity and maintain an arc about 23 ft. (7m.) long. They give an NO concentration of about 2.25 per cent and a yield of 550 to 575 kg. per kw-year or 65 grams per kw-hr.

*Pauling Process.* The Pauling furnace (Fig. 4) establishes an a-c. arc of 4000 volts between two curved horns much after the pattern of the horn type lightning arrester. This arc when established is driven upward by a blast of air admitted at *B* and is disrupted by the diverging horns. A sheet of arc flame is maintained by re-establishing a new arc as the previous one is elongated. The effect is to create an arc flame about 30 in. (75 cm.) high and to have this flame in intimate contact with

the rapid moving air used to blast the arc flame. Two furnaces are usually operated together and to assist in a rapid cooling of the products a portion of the previously heated or partially cooled discharged gases are admitted to the top of the furnace. The arc is established by the high voltage breaking down the gap between narrow blades *C* located in the horn gaps, and as these wear away they are continually advanced by the adjustments *D*. The percentage of NO obtained is 1.25 to 1.5 per cent in the 400 kw. furnace while the yields are 525 to 540 kg. per kw-year or 60 grams per kw-hr.

*Power Factor and Electrode Wear.* In all these processes where the arc is distorted the power factor is about 70 per cent being about 5 per cent lower in the Schonherr type, apparently due to inductive effects of the iron pipe surrounding the arc. In both the Pauling and Schonherr furnaces the electrodes are adjustable and the air blast plays directly on the electrodes necessitating this adjustment and also means of easy renewals. The Pauling blades last less than 24 hours, the Schonherr electrode is a straight rod of iron and is fed upward as it burns away. The Eyde water-cooled copper pipe not being directly in the path of the air blast lasts three to four weeks. In the operation of both the Eyde and Schonherr furnaces a furnace is placed on each separate leg of the three-phase circuit so that six wires are used for each generator. In the installations that have been made the furnaces are connected direct without transformers, and as no parallel operation of generators is attempted a large number of cables are required between the power house and the furnaces.

*Efficiency and Losses.* It will be noted that notwithstanding the radically different types of these furnaces there is not a wide divergency in the yields, the Schonherr furnace showing the highest concentration of NO while the Eyde probably produces a slightly higher output per kw-hr. All of these concentrations indicate that the maximum temperature of the arc is not utilized but is very considerably reduced by the large amount of air admitted. If the temperature of the arc is raised by admitting less air there is a heavier decomposition of the products and all products are heated to a higher temperature with a corresponding loss, the net result being a lower yield per kw-hr. As the yield per kw-hr. is of fundamental importance, adjustments are governed accordingly. The concentration of NO effects directly the apparatus for recovering the products, such as the absorb-

ing towers, and the lower the concentration of NO the greater the losses from heating the inert gases. The furnace efficiency will largely be determined by this factor. Let us take for example a concentration of 1.75 to 2 per cent NO and examine the distribution of heat. If we take the specific heats of a molecule of the diatomic gases as constant, there will be no difference in the specific heats per molecule of N, O or NO, and taking a standard value for this we may calculate the heat energy expended. Let us assume, following Haber, that for a change of temperature  $t$ , the specific heat per molecule will be

$$6.8 + 0.0006 t$$

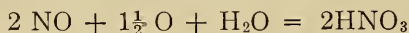
The gaseous products heated in the furnace with 1.75 to 2 per cent NO concentrations will have, from Nernst constants, an absolute temperature of about 2500 deg. and the air would have an initial temperature say of 27 deg. cent. or 300 deg. absolute, so the arc would raise the temperature of the 100 molecules through 2200 deg., or,

sensible heat =

$$100 (6.8 + 0.0006 t \times 2200 \text{deg.}) 2200 \text{ deg.} = 1,786,400 \text{ calories.}$$

As two molecules of NO require a latent heat of formation of 43,000 calories, the total heat will be 1,829,400 gram-calories; and as one watt hour equals 860 gram-calories the energy represented will be equal to 2.12 kw-hr. for two gram-molecules of NO. Taking the atomic weight of N as 14 and of O as 16, the gram-molecule of NO will weigh 30 grams, so 2.12 kw-hr. will form 60 grams of NO.

If we mix this NO with air and water it will form nitric acid without requiring a further expenditure of energy, thus,



and the 60 grams of NO will then become 126 grams of  $\text{HNO}_3$ ; the production of nitric acid will then be 126 grams per 2.12 kw-hr. or 59.4 grams of  $\text{HNO}_3$  per kw-hr. Of this expenditure of 2.12 kw-hr. the formation of the nitric oxide utilized

$$\frac{43000}{1,829,400} = 2.35 \text{ per cent,}$$

and the sensible heat imparted to the active gases to raise

their temperature to form two molecules of NO required 35,728 calories, so this represented

$$\frac{35,728}{1,829,400} = 1.95 \text{ per cent,}$$

while the heating of inert nitrogen and oxygen or that portion of the air which was not utilized but which was heated to the furnace temperature was represented by

$$\frac{1,750,672}{1,829,400} = 95.7 \text{ per cent.}$$

These calculations while open to some criticism on account of the uncertainty of the figures for specific heat and its change with temperature, closely approximate the conditions, and indicate that low concentrations of NO when formed from thermal reactions are extremely wasteful. If concentrations of 10 per cent NO are obtained with temperatures of 4200 deg. to 4300 deg. cent. the yields may be increased to 135 to 140 grams of  $\text{HNO}_3$  per kw-hr., but the greatest saving in energy will result in utilizing other than purely thermal energy. While thermal energy may be produced more cheaply directly from fuel, its temperature possibilities are again limited by the inert gases of combustion if air is the source of these.

Hausser has commercially applied a process for utilizing coke oven gases by means of an explosion bomb. The amounts of excess gases may be limited and the intimate mixture of combustible and oxygen due to pre-compression of the charge permits of high combustion temperatures being reached. Fig. 5 shows this bomb having a capacity of 1600 cu. cm. The gases, either illuminating or coke oven gases, enter through the inlet after previously exhausting the air by means of the air pump outlet. Means are provided at *A* for injecting under high pressure a spray of water to cool the products as quickly as possible. The ignition takes place at 2 by means of a high-tension spark and the explosion is propagated outward from this point and the vapor condenses on the enamel lining of the bomb.

With this device Hausser obtained a temp of 2100 T and concentrations of NO of 0.5 per cent. The temperature calculated from the assumed figures for specific heat indicated a concentration of 0.3 per cent for equilibrium by the Nernst calculation and Hausser sought to explain this increase of yield

as due to a chemical reaction induced by photo-chemical effects similar to the ionization by ultra-violet or actinic rays of light. The maximum yields were 99 grams of  $\text{HNO}_3$  per cu. m. of gas, or equivalent to 6.2 lb. of  $\text{HNO}_3$  per 1000 ft. of gas. A commercial plant on this system has been installed in Germany. This low concentration of NO greatly complicates the commercial application as the absorbing devices are more cumbersome and the percentages of loss are higher.

*Method of Utilizing NO.* All of the above nitric acid processes utilize the reaction

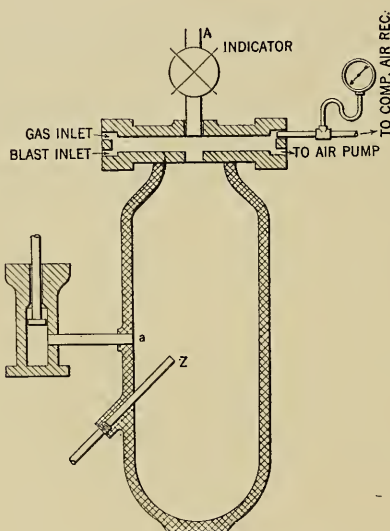
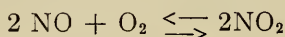
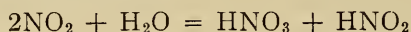


FIG. 5—HAUSSER PROCESS

which is an exothermic one for the formation of the peroxide, and if the temperatures are controlled, side reactions can be prevented and equilibrium can be maintained with only a small percentage of NO remaining. The gases after leaving the furnaces are usually carried through waste heat boilers where 50 to 60 per cent of the heat is utilized for steam production. They are then cooled in aluminum pipe coolers and allowed to enter a gas holder where time is given to form the peroxide. The products then enter counter current absorption towers where the reaction with water forms





the nitrous acid  $\text{HNO}_2$  is further oxidized and utilized to form  $\text{HNO}_3$  in contact with the excess oxygen in the gases and with the absorbing water. The final recovery is usually made by circulating the gases through two towers of weak alkaline solution, such as sodium carbonate and this is converted into sodium nitrate and into sodium nitrite, and recovered by evaporation, the final products are a combined nitrate-nitrite of sodium. A normal circulation over three absorbing towers gives an acid of about 30 per cent concentration but this can be increased to 45 or 50 per cent by recirculating over the first tower. Further concentrations are usually made by evaporation. All of these processes are simplified by increased concentrations of NO in the initial reaction. About two to three per cent of the original NO is discharged in the waste gases from the absorbing towers. It will be noted that one great advantage of these processes is that they require the handling of only air, gas and water up to the time the nitric acid is formed in the absorbing towers, so that the simplest handling devices suffice, and the labor is a minimum, also no chemicals are required until the final washing with the alkaline solution in the absorbing towers, and this may be a cheap solution such as lime water if conditions make it desirable.

*Cyanamide Process.* The very low yields, representing less than 5 per cent of the energy expended and amounting to 65 kw-hr. per kg. of N fixed, naturally have turned attention to chemical reactions as a means of increasing the yields. One of the most important of these is the process for making cyanamide  $\text{CaCN}_2$ . As a separate paper is to be presented here covering this subject, we will only generalize.

The endothermic reaction and the heating of the materials entering into the calcium carbide reaction have an approximate theoretical value of 3.1 kw-hr. per kg. produced, whereas it requires about 4 kw-hr. to produce a kg. of 85 per cent calcium carbide in the best practise. For 100 per cent carbide it would require 4.7 kw-hr. and the efficiency is therefore,

$$\frac{3.1}{4.7} = 66 \text{ per cent.}$$

The union of carbide and nitrogen is exothermic when a sufficient temperature is reached so the actual expenditure of energy for this reaction is not in excess of 0.1 to 0.2 kw-hr. additional for the fixation of the nitrogen. We require further the preparation

of the nitrogen, and the grinding of the carbide to prepare it for the nitrogen treatment. The cyanamide can be used directly in the fertilizer industry, but for use in the chemical industries it must be decomposed to form ammonia, or if nitric acid is required it must be made from the ammonia by some process such as the Ostwald contact process. We may figure however, that the yield for a given amount of electric energy which amounts to about 16.6 kw-hr. per kg of N fixed, is from four to five times the yield of the direct nitric acid processes, while offsetting this is the cost of preparing the nitrogen, the cost of chemicals, the handling of materials at high temperature, and the many factors making up manufacturing costs.

*The Serpek Process.* The Serpek process is typical and has been quite extensively introduced commercially. The reaction is represented by the equation



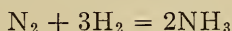
The reacting temperature for best results is claimed to be 1800 deg. to 1900 deg. cent., but no effort is made to define the equilibrium conditions and it is very evident that where CO enters so actively into the reaction the temperatures can be materially altered by a change in the partial pressures of the N and CO. One of the most interesting features of this process is that the impure  $\text{Al}_2\text{O}_3$  in the form of bauxite is fed into the furnace together with coal and the sensible heat is therefore partially derived from the coal. Neglecting the specific heats of the solids, the endothermic reaction requires three kw-hr. per kg. of aluminum nitride, having an approximate content of 26 to 34 per cent N; it would require therefore 9 to 10 kw-hr., per kg. of N under the best conditions if the coal and producer gas were capable of supplying all the heat energy required to produce the required temperature in the gaseous and solid products. In the case of cyanamide it requires about 4 kg. of high grade carbide per kg. of nitrogen or a kg. of N requires 16 kw-hr. under favorable conditions and about 0.2 kw-hr. for heating the carbide against 10 to 12 kw-hr. in the Serpek process. If all energy were supplied from the electric source the Serpek process would require practically the same electrical energy as the cyanamide process.

There is a distinct advantage in being able to use producer gas in place of preparing purified nitrogen and there is a further advantage in conducting the process with one operation. In

practise Serpek uses a revolving barrel furnace of the resistance type the resistance consisting of a squirrel-cage construction which continually agitates the material as it passes through. In all nitridereactions this is essential, as the materials become coated with a covering which protects the interior and prevents further absorption of nitrogen. Serpek feeds bauxite and coal from a producer type of furnace into this revolving electric furnace and the sensible heat is thus utilized to heat the material as it travels to the electric furnace the product is discharged from the electric furnace as aluminum nitride with a content of 26 per cent to 34 per cent N.

The aluminum nitride can be treated with steam and the N converted into ammonia or the ammonia may be converted into nitric acid. Serpek claims a process for converting the nitride directly into nitric acid but no details are available. One drawback to using Bauxite is that the resulting aluminum oxide is more difficult to use than the impure bauxite and the process does not work as economically, it is probable that some cheap catalytic agents may be found to substitute for the bauxite but otherwise the Serpek process should necessarily find its greatest application in connection with the reduction of aluminum.

*Haber-Catalytic Process.* One other process which has attracted marked attention on account of the scientific eminence of its inventor as well as the commercial results obtained is the Haber process for the synthesis of ammonia directly from its components N and H. This means that there must be a supply of these elements available or they must be cheaply produced. The reaction is an exothermic one producing 11,000 calories per gram-molecule so the problem is not so much the energy consumption as the peculiarities of the reaction



The ammonia formed is practically decomposed at 750 deg. cent. it has been difficult to get any substance to react with the N at this low temperature, and while the nitrogen was made active toward many substances it was easy to decompose the resulting  $\text{NH}_3$  into its constituent molecules and all yields obtained were too low to justify commercial results. Haber's success seems due more to ingenuity in constructing his apparatus and to the discovery of a suitable catalyzer than to any departure from previously known principles. The fact that one

molecule of N and three of H form only two molecules of ammonia indicates that the volume occupied by the ammonia will occupy only one-half the space occupied by its constituent gases and hence this contraction of volume will be assisted by pressure. Haber increased the pressure on the reacting gases to 200 atmospheres, and as a catalyzer he used uranium. He found at 500 deg. cent. he could react on the nitrogen and upwards of 8 per cent of ammonia could be formed before equilibrium took place. By using limited amounts of N and an excess of H the equilibrium pressures were adjusted well within the decomposition limits of temperatures and by withdrawing the gases from the catalyzer as they reached equilibrium the process was made continuous. The fact that decomposing ammonia creates a most destructive corrosive agent had to be met and the retorts had to be made strong enough to stand the effects of the high pressure, and also possible explosions, as hydrogen compressed to 200 atmospheres and heated to 500 deg. cent. is a most active agent in the presence of impurities such as oxygen, sulphur, etc. The retorts can be made of very moderate size, and a number of them used and by heating internally with electric resistance the shells are not subject to the effects of temperature, so the process seems to have met with very pronounced technical success. The consumption of energy for heating the gases is very slight as the exothermic reaction will compensate largely for the heat required to release this.

The preparation of the N and H and the compressions to 200 atmospheres will represent the greatest costs of production. It will be noted that all products are handled in the gaseous condition, being most favorable for low labor costs. The ammonia is extracted from the mixture of N and H by slightly cooling the gases until the point of liquefaction of ammonia is reached and the ammonia condenses out. The remaining gases are passed back to the retort without sacrificing the original pressure of compression. The work done on the gases is thus reduced to a minimum and equilibrium can be continually disturbed by withdrawing the products without heavy losses. This process involves the expenditure of approximately 1.5 kw-hr. per kg. of N and therefore represents the lowest consumption of energy of any of the fixation processes.

From an engineering point of view the various processes must be considered from other than the technical standpoint, the question of particular application being the guiding consideration in most cases.



## IV—THE ECONOMICS OF NITROGEN FIXATION

*Fertilizers.* In considering nitrogen fixation and its relation to fertilizers we must remember it is only one of the three important ingredients of fertilizers, the other two being phosphorous and potassium. It is possible to obtain nitrogen from the atmosphere and transfer it to the soil by means of nitrifying bacteria which may be cultivated by such plant life as the legumes, to which family belong the clover and alfalfa. These plants have a nodule on the stem which is the seat of the bacteria activity and if the plants containing this nitrogen are returned to the soil the soil may be enriched in nitrogen, but the crop must be sacrificed or partially so. When it is not desirable to plant these nitrifying crops recourse must be had to nitrogen in the form of fertilizer. Unfortunately all crops deprive the soil of fertility, and in the case of phosphorous and potassium converted into the crops, these must actually be replaced, or barren soil will eventually result. Each soil must be treated for the particular crop it is to bear and usually there are fixed mixtures which become standard for various crops. These mixtures contain the nitrogen the phosphorous and the potassium in varying amounts. The output of nitrogen from a chemical works would ordinarily be shipped to these fertilizer manufacturers unless the chemical works desired to manufacture the mixed fertilizers.

Of all the processes we have considered the cyanamide is the only one which manufactures a product which is in a form to go into the fertilizer market direct. The nitric acid processes must unite the acid with some alkaline base such as sodium, lime or ammonia and the ammonia processes must unite the product with an acid such as sulphuric or nitric. The nitride processes can hardly afford to ship the nitride, as it is combined with an ore or base such as aluminum oxide which may be more desirable in the aluminum industry, as the fertilizer industry will pay only on a nitrogen basis.

*Prices of Nitrogen.* In general the price of combined nitrogen as we have seen, is fixed by the price of Chile nitrate. Thus if this sells for two cents per lb. and contains 15 per cent N the price per lb. of N is 13.2 cents and this in turn would make the price of ammonia sulphate having 21 per cent of nitrogen 2.7 cents per lb. These have been current prices. In considering the production of nitrogen products, it would seem that while these prices control nitrogen for the fertilizer industry,



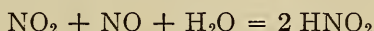
it would be desirable to produce if possible products which are manufactured from these crude products, and thus avoid competition with the natural products direct. Nitric acid of commerce is manufactured from soda nitrate by treatment with sulphuric acid, about 72 per cent of the sodium nitrate being nitric acid. As the by-products of this operation only partially pay the costs, the manufacturing costs leave the nitric acid with a value of 50 per cent over the value as nitrate. Hence a chemical works could afford to produce nitric acid when they could not afford to add a manufacturing cost to produce a fertilizer from the nitric acid and then sell it in competition with the crude Chile nitrate.

A large portion of the phosphate rock of this country is treated with sulphuric acid to form the so-called super phosphates. If nitric acid is used in place of sulphuric acid the super phosphate can be produced at the same time as a fertilizer of lime nitrate, or if preferred a high concentration of phosphoric acid can be produced from lower grade phosphate rock. Industries of this kind promise more favorable results commercially than does the direct production of fertilizer. If low grade products are manufactured at close prices a very large volume of business is a necessity and works of this character and magnitude are more apt to be a result of successful development rather than an initial venture in a field beset with uncertainties as to the profits and the chances of a development of other processes reducing these if they are problematical.

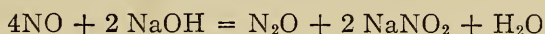
*Costs of Making Products.* Let us consider more in detail some of the costs. We may assume approximately that the labor and repairs in furnace room and absorbing tower will cost \$10 per ton of nitric acid and if nitric acid is selling for \$60 per ton, we have a margin for power cost, interest, general expense, etc. of \$50, and if we produce 500 kg. of acid per kilowatt year it will require two kw-yr. per metric ton or \$25 per kilowatt-year, and we must absorb all interest charges and general expense in this. If the yield can be made 550 kg. per kilowatt year and we can sell for \$60 per short ton, we will require 1.8 kw-yr. or \$28 per kw-yr. We must assume that the product does not have to be packed for shipment and that there are no selling costs involved, and we must figure on an output so that our units may be large enough to bring the investment in plant down to \$80 per ton of acid so the annual charge may be \$8 or net \$20 per kilowatt-year, and if \$5 are

allowed for general expense the best we can do will be about \$15.00 per kilowatt-year.

We see it would be hopeless to attempt to put this acid into a product to compete with the fertilizer prices, for they are some 50 per cent lower in selling price, and it will involve a cost for some raw material to mix with the acid, the cost of manufacture and a packing and shipping charge. We must then abandon any idea of making fertilizer from nitric acid prepared by the direct oxidation of atmospheric nitrogen in the electric arc until such time as we can improve the very low efficiency due to the thermodynamic limitations of the reaction. We can only hope to utilize this process in the manufacture of nitric acid coupled with some other product which will procure for it a higher price. There is for example a limited demand for the nitrite of sodium  $\text{NaNO}_2$  used in the dye industry and this is manufactured by reducing nitric acid with molten lead thereby adding another manufacturing operation to the acid cost. This nitrite may be cheaply made by taking a mixture of  $\text{NO}$  and  $\text{NO}_2$  such as we would have in parts of the system and passing it into water or sodium hydroxide, thus



or,



and this process would produce a product selling for four to five cents per lb. We must remember, however, that the price of nitric acid is not a fixture and that a cheap combined nitrogen fertilizer will cut the price of sodium nitrate and hence the price of nitric acid. We are confronted then with the fact that all processes will be affected by the success of any one process that is a large enough success to affect the market conditions of combined nitrogen and upset the ruling prices in the fertilizer industry. It is useless to look only to cheap power as a solution of this problem as the real solution is in the improvement of processes.

Let us roughly compare the power requirements of the processes as we have outlined them above and we find

Direct oxidizing of atmospheric nitrogen 5 per cent. efficiency, yield at 550 kg. per kw-year, requires per kg. of N.....	65 kw-hr.
Cyanamide process 66 per cent. efficiency in carbide 1 per cent. loss in heating to combine with N., requires per kg. of N,.....	16.6 "
Also preparation of N.	

Aluminum nitride using coal to heat products to temperature of reaction requires per kg. of N.....	12	kw-hr.
Catalytic method of combining N and H to form ammonia, requires per kg of N.....	1.5	"
Also preparation N and H, refrigeration, and compression to 200 atmospheres.		

The general tendency abroad in figuring the cost of water power is to give only the operating costs and from this one sees costs of producing power figured at from 50 cents to \$1.00 per kilowatt year and in using these figures erroneous ideas have been widely circulated. In this country it has been standard practice to consider the investment in the power plant, that is, the cost of the development and the property, as fixing very largely the cost of producing the power. It is quite common to have labor and supplies cost not more than one dollar per kilowatt-year, but this would not be considered as representing the cost of the power. Where a chemical industry owns the hydroelectric power plant as well as the chemical works, the foreign practice is inclined to consider the investment as a whole and apportion the costs of operation to the various departments, while interest on the capital is charged to the profits. The costs of producing power are therefore uniformly much lower than we are accustomed to figure on. There are many plants in operation in the chemical industries abroad whose real costs of producing power are no lower than many of the more favored locations in this country.

*Off-Peak Loads.* One of the chief interests in the chemical utilization of electrical energy is, centered in the possibilities of off-peak or off-season loads, as American plants generally have a certain proportion of power which can be disposed of to better advantage than selling the entire output as low priced power to chemical industries. This off-peak power is difficult to utilize in furnace work, where the cooling of the furnace and its charge is an important factor both from the standpoint of cost and of output, and again, adjustments may be so disturbed from an interrupted output as to be absolutely impracticable. One of the possible solutions for off peak utilization appears to be in the adoption of some system where fuel is also utilized and the radiation losses are not excessive under conditions of banked fire when the electric portion of the heat energy is not in use. Some of these combination processes may promise a solution of the off-peak load situation more attractive than the straight

electric furnace, which is difficult to cool down entirely without unduly affecting the conditions. In all plants the volume of output is the determining factor in absorbing the general overhead charges, and any intermittance must diminish output with its accompanying disadvantages.

If the furnace could be operated on the off-season load and its product stored, and the chemical works utilizing this product could operate on a normal schedule, this would form one solution; or another would be if by chance the off-season power were available at the time the greatest demands were to be met, such as preparing a fertilizer product at the season of fall rains for the early spring delivery. All of these plans however suggest the necessity of operating at least a portion of the plant continuously in order to meet fixed charges and preserve an operating organization. If the chemical works requires a moderate amount of power for its processes in year around operation and only its surplus for manufacturing its crude material at the off season peak it promises the greatest possibilities.

The future of nitrogen fixation is alluring and promises, many developments along lines other than those we have considered, but already the market has felt the effects of these various processes and instead of nitrogen being figured at thirteen cents per pound, it is confidently predicted it will very shortly find its level at a selling price of about eight cents, making a cost of production of five to six cents per pound and thus reducing sodium nitrate to about 1.33 cents per pound, or approximately \$30 per long ton, and the lower grade mines will feel this and be forced to curtail.

It therefore seems very certain that before 25 years shall have elapsed since Sir Wm. Crook's made his memorable address, the Chile nitrate beds will have vastly curtailed their production, not from exhaustion but from the inroads made by the onward advance of chemical and electrochemical engineering.

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